The Effect of Sodium Dodecyl Sulfate on Methane Gas Solubility in the Presence and Absence of Gas Hydrates

By

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Abstract

Over the years, methane hydrates have been intensely investigated for their vast potential as a future energy source and hazard to global climate. Sodium dodecyl sulfate (SDS), a hydrate promoting surfactant, was proven to increase the ethane hydrate formation rate by more than 700% (Zhong and Rogers, 2000). The mechanism proposed by Zhong and Rogers suggested the formation of micelles in the liquid bulk solution. These micelles are believed to create an environment for which ethane gas can be trapped within them, drastically increasing the solubility of the bulk, and in turn, increase the rate of hydrate formation.

An alternative theory, presented and published by Zhang et al. in 2008, proposed a different mechanism. They believed that the hydrate formation rate is increased by the greater negative potential introduced by SDS to the already negatively charged hydrate.

The purpose of this work was to determine which of the above two theories is most likely attributed to the drastic increase in hydrate formation. Experiments were first conducted with distilled deionized water in order to determine a baseline (control) and then with distilled deionized water and SDS at two different concentrations. The SDS concentrations tested were 31 ppm and 253 ppm, below and above the critical micelle concentration (CMC), respectively. Results show that the solubility of the bulk solution at a concentration of 31 ppm was equivalent to that of distilled deionized water alone. Furthermore, experiments show that at an SDS concentration of 253 ppm, the solubility at the onset of hydrate formation and in the presence of hydrates remains equal to that of distilled deionized water.

The results obtained from this work can only conclude that the theory stipulated by Zhong and Rogers is invalid due to the unaffected changes in solubility between distilled deionized water and distilled deionized water and SDS. Therefore, by default, the theory introduced by Zhang et al. is regarded to be the only accepted theory to date.
Abstrait

À travers les années, les hydrates de méthane ont été profondément étudiés pour leur abondante source d'énergie potentielle et le danger possible qu'ils représentent pour notre climat global. Il a été prouvé que le sulfate dodécylique de sodium (SDS), un hydrate favorisant l'agent tensio-actif, augmenterait le taux de formation d'hydrates d'éthane par plus de 700% (Zhong et Rogers, 2000). Le mécanisme proposé par Zhong et Rogers implique qu’il y a une formation des micelles dans la solution aqueuse. Il est estimé que ces micelles créent un environnement dans lequel le gaz d'éthane peut être emprisonné, augmentant considérablement la solubilité, et par le fait même, le taux de formation d'hydrates.

Une théorie alternative, présentée et publiée par Zhang et ses acolytes en 2008, propose un mécanisme divergent. Ces derniers ont supposé que le taux de formation d'hydrates est amplifié par le potentiel négatif supérieur introduit par le SDS à l'hydrate déjà négativement chargé.

Le but de ce travail était de déterminer laquelle des deux théories ci-dessus est davantage garantie de l'augmentation de la formation d'hydrates. Un premier lieu, des expériences ont été entreprises avec de l'eau désionisée distillée afin de déterminer une ligne directrice (contrôle) et ensuite avec de l'eau désionisée distillée et le SDS à deux concentrations différentes. Les concentrations de SDS testées étaient de 31 ppm et de 253 ppm, respectivement au-dessous et au-dessus du degré critique de concentration en micelle (CMC). Les résultats démontrent que la solubilité de la solution aqueuse à une concentration de 31 ppm était équivalente à celle de l'eau désionisée distillée. En outre, les expériences effectuées établissent qu'à une concentration en SDS de 253 ppm, la solubilité, en début et en instance d'hydrates, demeure similaire à celle de l'eau désionisée distillée, indépendamment des conditions d'opération utilisées.

Selon la résultante de ce travail, on peut en conclure que la théorie stipulée par Zhong et Rogers est invraisemblable dû au degré de solubilité inchangé entre l'eau désionisée distillée et l'eau désionisée
distillée additionnée de SDS. Par conséquent, par défaut, la théorie arborée par Zhang et ses collègues demeure la seule théorie plausible à jour.
Acknowledgments

The road to proudly obtain a masters degree in chemical engineering requires an extensive amount of discipline and commitment from an individual. However, most importantly, communication between yourself and many individuals within the department is the absolute key to success. Many of these individuals were of great help to me during the completion of my degree. It is for this reason that I would like to take this opportunity to sincerely thank all thous who have contributed and made this experience one of which I will cherish for the rest of my life. I would like to start by thanking my supervisor Professor Phillip Servio for all of his support. He not only provided guidance but challenged and motivated me to become the best I can be. I can honestly say that this dissertation would not have been possible without him. I would also like to thank Professor Milan Maric for his guidance and direction during my research. My research group for all their help, in particularly Mr. Hallavard Bruusgaard for always lending a helping hand whenever I needed it especially during differentials. Mr Frank Caporuscio for his outstanding laboratory skills. I can undoubtedly say that without him, the experimental set-up would not have such smooth functionality as it does today.

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1. Introduction

Clathrate hydrates or more commonly, gas hydrates, are non-stoichiometric crystalline compounds. Under correct thermodynamic conditions, a gas molecule accompanied by liquid water will combine to form a hydrate. The integrity of the hydrate structure is composed of two essential components. The first, is the outer structure or “cage” composed of water molecules held together by strong hydrogen bonding. The second, is a gas molecule or volatile liquid, also referred to as a “guest” molecule, enclosed in the hydrogen bonded cage. This gas molecule stabilizes the gas hydrate cage by weak van der Walls forces. Without the “guest” molecule, the integrity of the hydrate structure would be compromised and ultimately collapse into conventional water, releasing the enclosed gas into its corresponding gas phase.

Over the years, methane hydrates have been intensely investigated for its vast potential future energy source, and risk to global climate (Englezos, 1993; Kvenvolden, 1999). Furthermore, hydrates have been looked upon as a promising new means of transporting and storing natural gas instead of using the conventional high pressure liquid form. It has been proven to be more economical and a safer means (Benesh, 1942; Miller et al, 1946; Parent, 1948; Gudmundsen and Borrehaug, 1996) since the amount of space (volume) required at standard temperature and pressure is approximately 160 times more than would be required in hydrate form (Sloan, 2007) It has been estimated that approximately 53% of all carbon based resources available on earth are stored in hydrate form (Kvenvolden, 1988a) Thus, the amount of organic carbon trapped in hydrates exceeds all other reserves (fossil fuels, soil, peat, and living organisms) (Suess et al., 1999) Figure 1.1 provides an illustration of organic carbon available in Earth's reserves. Although hydrates seem to be an extremely promising future energy source, the consequences could be catastrophic. If global warming occurs, the atmospheric temperature will rise and decompose some of the Earths methane hydrates, inevitably releasing methane into the
atmosphere.

![Figure 1.1: Gas Hydrate Deposits in the World (adapted from Suess et al., 1999)](image)

It has been speculated that underwater landslides can occur if massive sub sea hydrate reserves are destabilized, producing devastating results to the earth's atmosphere (Suess et al., 1999). Furthermore, it has been estimated that the global warming potential of methane is 21 times that of carbon dioxide, a powerful greenhouse gas (Englezos, 1993). Figure 1.1, displays a map of all potential hydrate energy sources discovered around the world. To date, the main areas which contain the largest supply of hydrates include both the arctic permafrost regions (e.g. Siberian Coast), deep rivers (e.g. Mackenzie Delta in Canada) and deep sub-sea sediments (e.g. Arctic and Atlantic oceans). Although
the most common type of hydrate on earth is methane, carbon dioxide hydrates (CO$_2$) have also been investigated for their potential to be sequestered in deep sea ocean floors (Brewer et al., 2000). At present, it is well known that carbon dioxide, a significant contributor to global warming, is a major component in the emissions of thermal power plants. Following the climate convention in Kyoto in 1997, the United Nations established one of the most significant initiatives of its time with respect to climate change, the Kyoto Protocol. In essence, the pledge made by several countries including Canada, was to reduce the emission of carbon dioxide by 6% of the 1990 reported carbon dioxide level.

In order to abide by the protocol and improve atmospheric conditions, carbon dioxide from thermal power plants must be captured and safely disposed of. Therefore, if a means of sequestering the carbon dioxide gas in hydrate form and managed to be stored successfully in deep sea sediments, the rate of ozone depletion and global warming can be significantly reduced. At present, there are several issues hindering the initiation of such sequestration. One of which is the unfavourable kinetics and low conversion of water to hydrate (Lee et al. 2007). Overall, the hydrate formation rate is affected by several operating conditions such as the degree of supercooling (temperature), pressurization, speed of agitation of solution etc.

The addition of surfactants into such solutions has also been investigated to determine its promotion or inhibition effects. At the moment, the promotion mechanism effect between surfactant and gas hydration rate, is still yet to be fully understood. However, two distinct theories have been proposed. The first was proposed by Zhong and Rogers in 2000. They stated that sodium dodecyl sulfate (SDS), a hydrate promoter, was proven to increase the ethane hydration rate by more than 700% (Zhong and Rogers, 2000). They speculated that this large increase in hydrate formation was due to the formation of micelles in solution. At a critical micelle concentration (CMC) of 242 ppm or greater, 60 SDS molecules agglomerate to form a micelle, trapping an ethane molecule in its cavity (centre). Thus, the existence of these micelles are believed to dramatically increase the solubility of...
dissolved ethane in the liquid phase, which in turn, dramatically increases the hydrate formation rate. The second theory proposed by Zhang et al, 2008, involves the adsorption of SDS cation at the gas-liquid interface. Upon formation, gas hydrates naturally have a negative charge in the absence of any surfactant. However, the addition of SDS decreases the negative charge or zeta potential (more negative) as the SDS concentration increases from 0.17 mM to 3.4 mM, which in turn, dramatically increasing the hydrate formation rate (Lo et al, 2008; Zhang et al, 2008) At the moment, speculation between both theories exist and the determination of the appropriate theory is needed if further research is to be conducted to obtain better, more environment friendly hydrate promoters.

The purpose of this work was to determine which of the above two theories is more appropriate of a hypothesis. Due to lack of data presently available to determine the latter, experiments were conducted to determine the solubility of methane with the inclusion of SDS under hydrate and non-hydrate forming conditions. The results were then compared to an identical hydrate system in the absence of SDS (Servio et al, 2002) to determine significant differences in solubility, if any. For simplicity, the guest molecule used for all experiments in this work was methane gas.

1.1 Historical Background

Gas hydrates were first discovered by Sir Humphry Davy in the year 1810. Sir Davy managed to combine chlorine gas with water at a temperature of 282K, what he observed was the hydrate of chlorine, a crystalline structure resembling that of ice. Thirteen years later, a researcher by the name of Michael Faraday confirmed Sir Davy’s results. In his published paper, Mr. Faraday also concluded that for every chlorine molecule, 10 water molecules were required to form a hydrate crystal (Faraday 1823) Other forms of hydrate crystals such as methane, ethane and propane hydrates were later discovered by Mr. Villard in 1888 (Sloan, 2007)

It was not until 1934, that gas hydrates began to be extensively investigated. Prior to this, gas
hydrates were seen as purely academic research and were prepared mostly in small scale laboratories. Naturally occurring gas hydrates were first seen in the 1960's mainly on ocean floors and permafrost regions but remained between low to moderate importance. However, after the discovery of hydrate plugs in natural gas pipe lines, the demand for knowledge about these compounds and chemicals capable of preventing these plugs became extremely significant (Sloan, 2007) Figure 1.2 illustrates a pipeline plugged by gas hydrates.

![Pipeline plugged by Gas Hydrates](http://www.hydrafact.com)

**Figure 1.2:** Pipeline plugged by Gas Hydrates  
(Source: www.hydrafact.com)

Today, the amount of effort put forth in this field is enormous. University research laboratories can be found all over the world including China, Australia, Canada, United States of America, the United kingdom etc. As can be seen in literature, research on gas hydrates has been very diverse and can range from the determination of phase equilibrium of multi-component hydrate systems to promotion and inhibition effects. The field of gas hydrates is vast and will only continue to grow as knowledge expands.

### 1.2 Hydrate Structure

Hydrate structures have been investigated by researchers since the early 1950’s. Until now, three hydrate structures have been determined using x-ray diffraction. The first two were discovered in
1951 and in 1952 by von Stackelberg, Pauling and Claussen (A. V. Kurnosov et al., 2001) and were named “Structure II” and “Structure I”, respectively. It was not until 1987 that the third hydrate structure named “Structure H” was discovered (Sloan, 2007). The three hydrate structures each exist as a separate and distinct structure due to differences in forming conditions namely, temperature, pressure and type of “guest molecule” available.

Hydrate structures are composed of two distinctive features and are common in all three structures. The first, is the cage or lattice of the hydrate. It is formed by the strong formation of hydrogen bonds between water molecules, producing a cubic structure for type I and II while type H produces a hexagonal water lattice (A. V. Kurnosov et al., 2001). The second distinctive feature is the enclosure of a “guest” molecule. This guest molecule, which is typically a gas molecule, plays the key role of stabilizing the hydrate by the interaction of weak van der Waals forces between itself and the hydrogen bonded water lattice. For the latter to be true and to remain stable, the guest molecule must meet the specific size requirements of the lattice. On average, the guest molecule cannot be smaller than three Angstroms (3 Å). If the guest molecule happens to be smaller, the weak van der Waals forces between the guest molecule and the hydrogen bonded cage will not be sufficient for stability, thus compromising the integrity of the hydrate and ultimately decomposing into its constituent molecules. Although seldom, it is possible for a hydrate cage to entrap two guest molecules into one lattice. Due to the extremely small size of hydrogen or noble gas molecules, two of these molecules can squeeze into the lattice and stabilize the hydrate (Mao, W. L. et al., 2002).

1.2.1 Structure I Hydrates

Cubic structure I hydrates are predominantly found in the earth’s environment. It occupies the smallest “guest” molecule of all three structures. The “guest” molecular size range is typically between 0.4-0.55 nm (nanometers). Examples of molecules in this range are methane, ethane, carbon dioxide,
hydrogen disulfide etc. Forty six (46) water molecules, the basic building block of the hydrate structure, hydrogen bond together by forming two possible geometries. Depending on the environmental conditions/operating conditions and “guest” molecule available, a pentagonal dodecahedron \(5^{12}\) and tetrakaidecahedron \(5^{12}6^2\) will form. The nomenclature \(5^{12}\) and \(5^{12}6^2\) denotes the following,

\[
5^{12} = \text{A geometry composed of twelve (12) pentagonal faces} \\
5^{12}6^2 = \text{A geometry composed of twelve (12) pentagonal faces and two (2) hexagonal faces}
\]

Figure 1.3 illustrates the geometry of both the pentagonal dodecahedron and the tetrakaidecahedron. It is noteworthy to mention that of the geometry’s available for structure I hydrates, the tetrakaidecahedron is larger then the pentagonal dodecahedron i.e. a larger cavity for the guest is formed. Therefore, the larger molecules available for structure I hydrates will occupy the tetrakaidecahedrons. However, for a unit crystal of hydrate structure type I to exist, two \(5^{12}\) cages, six \(5^{12}6^2\) cages and 46 water molecules must all bond together. If a “guest” molecule is too large to occupy the smaller geometry available for structure type I, the smaller cages, namely the \(5^{12}\) cage, will remain unfilled as the hydrate unit cells are formed. However, small “guest” molecules are able to occupy both the smaller and larger geometries of the hydrate. The same also holds true for hydrate structure type II and H. Typically, the concentrations between water and “guest” molecule is approximately the same for all three structures, namely 85 mol % water and 15 mol % “guest” (Sloan, 2007). Figure 1.3 and Table 1.1 illustrate the unit crystal of type I, II and H along with supplemental information about each structure.

### 1.2.2 Structure II Hydrates

Cubic structure II hydrates are usually found in man made environments; such as, laboratories in academic units. This structure occupies average sized “guest” molecules from the available three configurations. The “guest” molecular size range is typically 0.6-0.7 nm. Examples of such molecules
are propane and iso-butane (Sloan, 2007) Although most are in the typical range stated above, the smallest molecules available (< 0.4 nm) will also form type II hydrates. The reason, is due to the cavities produced. When compared to structure I hydrate, the smaller of the two cavities produced in structure II hydrate, is still relatively larger then the smaller cavity produced by the structure I hydrate. Therefore, it is more stable for molecules of < 0.4 nm for instance, Kr, Ar, O₂ and N₂ to form structure type II hydrate then type I (Sloan, 2007). One hundred and thirty six (136) water molecules, hydrogen bond together to form two possible geometries. Depending on the operating conditions and “guest” molecule available, a pentagonal dodecahedron ($5^{12}$) and hexakaidecahedron ($5^{12}6^4$) will form. The nomenclature $5^{12}$ and $5^{12}6^4$ denotes the following,

$5^{12}$ = A geometry composed of twelve (12) pentagonal faces
$5^{12}6^4$ = A geometry composed of twelve (12) pentagonal faces and four (4) hexagonal faces

Figure 1.3 illustrates the geometry of both the pentagonal dodecahedron and the hexakaidecahedron. It is noteworthy to mention that of the structures available for structure II hydrates, the hexakaidecahedron is larger then the pentagonal dodecahedron. Therefore, the larger molecules available for structure II hydrates will occupy the hexakaidecahedron. However, for a unit crystal of hydrate structure type II to exist, sixteen $5^{12}$ cages, eight $5^{12}6^4$ cages and 136 water molecules must all bond together. A summary along with additional information is available in Table 1.1

1.2.3 Structure H Hydrates

Hexagonal structure H hydrates are found in both natural and man made environments such as, laboratories in academic units and deep sea sediments. Primarily, the difference between structure H and structure I and II is the molecular occupancy. Type H hydrates will only exist in combination of both large and small “guest” molecules. Its occupancy is specifically for large sized “guest” molecule(s). The “guest” molecular size range is typically 0.8-0.9 nm. Examples of such molecules are methane + neohexane, methane + cycloheptane, adamantane, cycloalkain, etc. (Sloan, 2007) Thirty four
(34) water molecules, the basic building block of the hydrate structure, hydrogen bond together to form three possible geometries. The three geometries available for the hydrate structure H are the pentagonal dodecahedron \( (5^{12}) \) (also available for structure type I and II), the \( 4^{3}5^{6}6^{3} \) geometry and finally, the \( 5^{12}6^{8} \) geometry. The nomenclature \( 5^{12}, 4^{3}5^{6}6^{3} \) and \( 5^{12}6^{8} \) denotes the following,

\[
\begin{align*}
5^{12} & = \text{A geometry composed of twelve (12) pentagonal faces} \\
4^{3}5^{6}6^{3} & = \text{A geometry composed of three (3) square faces, six (6) pentagonal faces and three (3) hexagonal faces} \\
5^{12}6^{8} & = \text{A geometry composed of twelve (12) pentagonal faces and eight (8) hexagonal faces}
\end{align*}
\]

Figure 1.3 illustrates the three geometries of the hydrate structure H. It is noteworthy to mention that of the structures available for structure H hydrates, the \( 5^{12}6^{8} \) non-spherical configuration is largest of the three, while the \( 5^{12} \) and \( 4^{3}5^{6}6^{3} \) are both considered as small cavities. Therefore, the larger molecules available for structure H hydrates will be enclatherated in the \( 5^{12}6^{8} \) geometry. However, for a unit crystal of hydrate structure type H to exist, three \( 5^{12} \) cages, two \( 4^{3}5^{6}6^{3} \) cages, one \( 5^{12}6^{8} \) cage and 34 water molecules must all bond together. Unlike structure I and II hydrates, the stability of structure H hydrates requires two separate molecules of different sizes to occupy the vacancy (Sloan, 2007) A summary along with additional information is available in Table 1.1.
Table 1.1: Additional Information on Gas Hydrates (Sloan, 2007)

<table>
<thead>
<tr>
<th>Hydrate Crystal Structure</th>
<th>I</th>
<th>II</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cavity</td>
<td>Small</td>
<td>Large</td>
<td>Small</td>
</tr>
<tr>
<td>Description</td>
<td>$5^{12}$</td>
<td>$5^{12}6^2$</td>
<td>$5^{12}$</td>
</tr>
<tr>
<td>Number of Cavities per Unit Cell</td>
<td>2</td>
<td>6</td>
<td>16</td>
</tr>
<tr>
<td>Average Cavity Radius (Å)</td>
<td>3.95</td>
<td>4.33</td>
<td>3.91</td>
</tr>
<tr>
<td>Coordinator Number*</td>
<td>20</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>Number of Waters per Unit Cell</td>
<td>46</td>
<td>136</td>
<td>34</td>
</tr>
</tbody>
</table>

* Number of oxygens at the periphery of each cavity.

$^+$ Estimates of Structure H cavities from geometric models.

1.3 Thermodynamics – Hydrate Formation and Equilibrium

As previously discussed in this report, the study of gas hydrates can be subdivided into many categories. However, to truly understand the concepts and reasoning involved in its scientific research, the basics of thermodynamics must first be well understood. Without it, simple concepts such as hydrate formation, stability, equilibrium, hydrate kinetics, driving forces, mole fractions, solubility and the determination of adequate operating conditions can be easily misinterpreted and possibly lead to incorrect or invalid conclusions. Therefore, the following subsections introduces some key thermodynamic concepts needed for the understanding of this research.

1.3.1 Incipient Hydrate Formation

The term incipient refers to “the minimum amount required” for a specific process to occur. When considering gas hydrates or the incipient hydrate formation conditions, the term refers to the minimum operating conditions required to produce an infinitely small amount of hydrates. To date, the incipient conditions for many hydrate systems including mixtures have been studied extensively.

The first researchers to conduct proper experimental procedures and determine the incipient hydrate forming conditions were Deaton and Frost in 1946. The method employed was referred to as
“the isothermal pressure-search method” Setting the hydrate forming system at a specific temperature, the pressure was incrementally increased until the formation of hydrates was observed. Theoretically, if the pressure in the hydrate forming system is increased very slowly and left to settle for an infinite amount of time (equilibration), the pressure at which the formation of hydrates is observed, is the equilibrium pressure at that specific temperature. However, in all practicality this is not the case. For the formation of hydrates to be observed, their must exist a driving force. This driving force is merely a measure of potential for the system to actually form hydrates. For example, suppose the intrinsic conditions to form hydrates at 4°C is a pressure of 4700 kPa. If the system is left at these conditions, the system will undoubtedly never form hydrates. The reason is because the driving force to produce hydrates is zero at equilibrium conditions. Although thermodynamics states that hydrates can exist under these conditions, the formation will never occur. In other words, thermodynamics simply states the conditions required for hydrates to exist. If the pressure in the system is increased by 1 kPa, to 4701 kPa and all other conditions remain constant, the driving force would be \( P_{\text{actual}} - P_{\text{equilibrium}} \) hence, \( (4701\text{kPa} - 4700\text{kPa}) = 1 \text{kPa} \). The system now has a driving force of 1 kPa to produce hydrates. Although 1 kPa is a very small driving force, the system still has a potential to form hydrates. The question now is not if hydrates will form, but in how much time. As mentioned above, thermodynamics only states the conditions required for hydrates to exist. At a potential of 1 kPa, the time required is impossible to predict and can be very long i.e an infinite amount of time and is thus impractical. However, if the driving force is increased by approximately 1000 kPa, the time required to form hydrates is significantly reduced and can form in approximately 1 hour or more. Again, this is attributed to the driving force being much higher. Once the formation of hydrates is observed, the system pressure must be readjusted to express the true equilibrium pressure. This is done by slowly reducing the pressure until the decomposition of hydrates is observed. The moment the observation is made, the temperature and pressure is recorded as an equilibrium condition. This procedure is then
repeated for several different temperatures until a partial phase diagram is obtained. It is worth mentioning that the above procedure could also have been performed in reverse order, by keeping the pressure constant and adjusting the temperature of the system. Unfortunately, this method would require more effort to obtain the same information due the time requirements for thermal and mechanical equilibrium to be reached.

1.3.2 Thermodynamics of Methane Hydrate

The conditions required for the formation of methane hydrates was first discovered by Dalton and Frost in 1946. Using the isothermal pressure-search method, the first partial phase diagram for methane hydrate was determined. Figure 1.4 below is the actual partial phase diagram published in 1946.

![Partial Phase Diagram for Methane-Water](adapted from Deaton and Frost, 1946)

**Figure 1.4:** Partial Phase Diagram for Methane-Water (adapted from Deaton and Frost, 1946)

From the plot, the y-axis states the pressure in kilo-pascals (kPa) while the x-axis states the temperature in Kelvin (K), of the respective phases. The plot is simply a parabolic line (three phase equilibrium line) which separates the two possible phases (Methane Hydrate & Liquid Water from Methane Gas & Liquid Water) and provides the correct thermodynamic conditions for each to exist.
When thermodynamic conditions are specified to be directly on the line, all three phases can co-exist, that is, Methane Gas, Methane Hydrate and Liquid Water (V-H-Lw, respectively) in equilibrium. Below this line, hydrates can not form hence, the two phases present are methane gas as a vapour and liquid water. Above the three phase equilibrium line however, methane hydrate and liquid water are present.

1.4 Kinetics of Hydrate Formation

The kinetics of hydrate formation is represented by three distinctive stages: dissolution, nucleation and growth. The dissolution stage is the dissolution of gas into the respective liquid phase i.e liquid water. The dissolution phase must reach two levels of saturation prior to reaching the nucleation step. As gas is continuously dissolved into the liquid, the liquid will reach a point at which the solution is said to be saturated. For the nucleation process to take place, the liquid must reach a level well beyond saturation. This level is identified as supersaturation. A supersaturated solution is thus, a higher concentration of gas dissolved into the liquid phase then normally would be under the same temperature and pressure and is therefore, not in equilibrium. Once the liquid is supersaturated, nucleation begins. Nucleation is defined as the formation and dissociation of hydrate clusters that are present in the liquid water phase. The latter process is said to continuously occur until the size of the hydrate cluster is large enough to form a nuclei. Once there are enough nuclei formed in the liquid, the growth of hydrate is initiated (also known as the turbidity point) and will continue to grow linearly until the liquid phase is transformed into hydrates (assuming the gas phase is available in abundance) Figure 1.5 illustrates the three stages of the kinetics of hydrate formation. From the graph, the time referred to as $t_{eq}$ is the onset of nucleation while $t_{tb}$ is the onset of visual hydrate growth. The difference between these two times i.e. $(t_{tb} - t_{eq})$ is know as the Nucleation Induction Period.
1.4.1 Hydrate Nucleation

Over the years, extensive research has been conducted on hydrate nucleation. The most promising work was conducted by Servio in 1998, for the determination that the nucleation process was stochastic i.e. a non deterministic process. Prior to this discovery, many researchers have managed to determine specific factors which affect nucleation. The five most significant are the following,

1) The History of Water or Memory Effect (Vysniaukas and Bishnoi, 1983)
2) The Stirring Rate (Englezos et al, 1987)
3) The Temperature and Pressure (Sloan, 2007)
4) The Molecular Diameter to Cavity Size Ratio (Sloan, 2007)
5) The Degree of Supersaturation (Bishnoi and Natarjan, 1996)

The history or memory effect of water was first reported by Vysniaukas and Bishnoi in 1983. They stipulated that if a system is left to form hydrates and allowed to decompose, the induction time required to reform hydrates (using the same water) at any condition, is significantly reduced. This reduction in induction time was thus attributed to the “history of water” or the “memory effect of
water” to easily reform hydrates. However, in April 2010, Wilson and Haymet reported that hydrate formation and reformation of water mixtures shows no evidence to support a “memory effect.” They determined that the “memory effect” results from water, which is obtained from decomposed hydrates, possesses a “modified” structure which allows easier hydrate re-formation (P.W. Wilson and A.D.J Haymet, 2010). In 1987, Englezos reported that if the stirring rate of water in a system is increased, the induction time is significantly reduced. In 1990, Sloan reported two key factors for reducing the induction time of nucleation. The first, was the production of hydrates at low temperatures and high pressures and secondly, the stability of the hydrates. He determined that the size of the guest molecule forming the hydrate had a significant impact on stability. Thus, the more stable the hydrate, the smaller the induction time. In 1996, Bishnoi and Natarjan concluded that the larger the dissolution of gas in the liquid beyond the point of saturation (higher degree of supersaturation), the shorter was the induction time.

1.5 Industrial Problems

The formation of gas hydrates can cause many problems in the oil and gas industry. Two of the most significant issues will be presented in this section. The first is the formation of hydrates in natural gas pipelines which has been extensively documented and dates back to the 1930’s (Sloan, 2007). During normal operating conditions, natural gas pipelines are known to operate at extremely high pressures. If outdoor ambient conditions (OAT) such as temperature drops below a certain value, the formation of gas hydrates may become favorable. If this occurs, hydrates would begin to form in the gas pipeline causing a hydrate plug and inevitably ceasing the flow of gas (see Figure 1.2). To date, hydrate plugs are of serious concern to the oil and gas industry. It has been estimated that approximately one hundred million dollars (100 000 000$) is spent annually for the prevention of gas hydrates for the overall industrial processes (Sivaraman, 2002). Once a hydrate plug has occurred in a
pipeline, the overall decomposition rate can be very slow. It has been estimated that when allowed to naturally decompose at -5 °C and standard atmospheric pressure i.e. at conditions well below the hydrate-liquid water-gas equilibrium line, the decomposition percentages at twenty four hours and one month were seven percent (7%) and fifty percent (50%), respectively (Shirota et al., 2002) Thus, the prevention of hydrate plugs must constantly be mitigated.

The second significant issue affecting the industry today are oil spills and the 2010 Gulf of Mexico oil spill by British Petroleum (BP) is an example of its catastrophic results. Gas hydrates may not have been the cause of the oil spill however, they have been blamed for the prevention of a successful tapering. The leak which steams form a gusher, located on the floor bed of the gulf of Mexico, was the result of an oil well blowout that occurred on April 20\textsuperscript{th}, 2010. The blowout, caused a massive explosion on the oil platform, killing 11 people and injuring 17 others (Welch, William; Joyner, Chris, 2010)

The first attempt, after failing to close the fail save valves located on the rig, was made on May 7-8\textsuperscript{th}, 2010. The idea was to place a 125 ton dome over the leak so that excess oil could be piped to a storage vessel waiting at the surface. However, due to such depths, as the oil came into contact with water, methane hydrates quickly formed and clogged the steel canopy at the top of the dome. Since the density of methane hydrates is less then that of water, the methane hydrates plugged the top of the dome where the connection was to be made for siphoning. After many attempts by BP to slow down or stop the leak, success finally prevailed on July 15\textsuperscript{th} 2010, by capping the leaking wellhead.

To date, the flow rate estimates provided by the United States Government (Federal Science) was approximately fifty three thousand barrels of oil per day (53 000 barrels/day) at the time the leaking gusher was sealed. Further estimates reveal the leak was at its greatest right after the explosion at approximately sixty two thousand barrels of oil per day (62 000 barrels/day) and slowly decreased due to the depletion of the hydrocarbon reserve (Robertson, Campbell; Krauss, Clifford, 2010) If an
economic and environmentally friendly gas hydrate inhibitor were commercially available, it could have potentially saved the environment from thousands of barrels of oil per day.

1.6 Hydrate Inhibition

Hydrate inhibitors i.e. the prevention of hydrate growth, has long been sought out for, particularly, by the oil and gas industry. If a process must operate in hydrate forming conditions, several different compounds can be added to the flow stream to inhibit hydrate formation and growth. Such compounds are, anti-freeze proteins (AFP) and anti-freeze glycoproteins which are both derived from fish and Poly(N-vinylpyrroidone-co-N-vinylcaprolactam) (poly (VP/VC) a polymer based compound (S. Al-Adel et al, 2008) Inhibitors can be divided into three separate classes;

1) Thermodynamic Inhibitors,
2) Kinetic Inhibitors,
3) Anti-agglomerates.

The mechanism by which thermodynamic inhibitors overcome hydrate production is by shifting the three phase equilibrium line (Lw-H-V) so that the process can tolerate higher temperatures and pressures then normally would.

Kinetic inhibitors simply help in decreasing the hydrate nucleation rate and growth while anti-agglomerates prevent the clustering of hydrate crystals. The latter is also referred to as Low Dosage Hydrate Inhibitors (LDHI) due to the extremely low dosages required for inhibition to occur when compared to thermodynamic inhibitors.

1.6.1 Thermodynamic Inhibition

Thermodynamic inhibition is the most traditional of all methods employed. Four possible ways exist for thermodynamic inhibition, they are:

1) Decreasing the system Pressure
2) Increasing the system Temperature
3) Removing excess water
4) Injection of a thermodynamic inhibitor

1.6.1.1 Decreasing the System Pressure

If permissible, the pressure of a particular system in question can be reduced so that the process can operate below the three phase equilibrium line (Lw-H-V) as previously stated in this report (See figure 1.4) Unfortunately, this method of inhibition can require additional equipment or partial isolation of already existing equipment, increased energy requirements etc. making it economically unfavorable to some processes (Sloan, 2007)

1.6.1.2 Increasing the System Temperature

Again, if permitted, the temperature of a particular system in question can be increased so that the process can operate below the three phase equilibrium line (Lw-H-V) as previously stated in this report (See figure 1.4) Unfortunately, this method of inhibition can require additional equipment such as heat exchangers, partial isolation of already existing equipment, increased energy requirements etc. which may disrupt up stream systems making it economically unfavorable to some processes (Sloan, 2007)

1.6.1.3 Removal of Water

The removal of water from a system will inhibit the formation of hydrates. For hydrates to nucleate and grow, water molecules must be available to form a water lattice and take on a guest molecule. However, if no water is available, the formation of the host lattice can not be obtained and thus, no hydrates will form. The removal of water, or the dehydration process, is usually performed before a process is allowed to begin. This in turn, will allow the dew point of the solution to be below
that of the operating temperature hindering any formation of water during operation.

The removal of water can also be performed by using other methods. If permitted, glycols can be used for dehydration however, many systems do not allow it due to possible disturbances in upstream process. Glycols are also limited under severe cold conditions, (below -40°C) as they become significantly ineffective. If removal of water is absolutely required at conditions below -40°C, molecular sieves or solid desiccants are usually used however, these can be extremely expensive.

1.6.1.4 Injecting a Thermodynamic Inhibitor

If the a systematic process permits, a chemical acting as an inhibitor can be injected to decompose or prevent the formation of hydrates. These chemicals interfere with formation process in two distinctive ways. The first, is by interacting with the free water molecules which are available for hydrate formation, disrupting their ability to form a lattice (Sloan, 2007) The second, is by destabilizing the hydrate lattice by acting as an ineffective “guest” molecule (Sloan, 2007) To date, the most readily available thermodynamic inhibitors are:

1) Methanol

2) Glycols; including monoethylene glycol (MEG), diethylene glycol (DEG), and triethylene glycol (TEG)

3) Electrolytic solutions

The inhibiting effect imposed by methanol is strictly due to intermolecular forces. The free water molecules, which are available to form a water lattice, have a higher affinity to bind with methanol then to form a hydrate, inhibiting its formation. Furthermore, the methyl group form the methanol molecule further inhibits the formation of hydrates by directly competing with other “guest” molecules. Under most circumstances, methanol is used under extreme conditions well below -40 °C due to its relatively low freezing point. However, its not uncommon for methanol to be used at conditions well above this, for example, in the gulf of Mexico during the 2010 oil spill. It should be
noted that although methanol is a very effective inhibitor, it is not an environmental friendly chemical as it can cause a high death rate in aquatic life.

Glycols can also be used as a hydrate inhibitor. Unfortunately, its inhibitor effects is not as efficient as that of methanol due to its larger chemical structure. D.E Sloan reported that generally, as the inhibitor molecular size increases, the inhibitor efficiency decreases (Sloan, 2007) Operating conditions for the use of glycols are primarily up to -40 °C. Beyond this temperature, the viscosity increase impedes its recovery via separation leading to adverse challenges and a potential increase in production cost. Of all glycols, MEG is the most widely used due to its low viscosity, low solubility in liquid hydrocarbons and low cost with respect to others (GPSA, 1998) TEG however, is seldom used due to its relatively low vapor pressure.

Electrolytes, the third inhibitor from the list above, also inhibits water from forming a hydrate lattice. Electrolyte solutions can ionize and form dipole-dipole bonds with the available free water and inhibit hydrate formation. The downside of such inhibition is the possible increase in corrosion on sensitive equipment therefore, consideration should be made if electrolytes are to be used.

Although the addition of a thermodynamic inhibitor may seem as a “perfect” solution to the prevention of gas hydrates, in some situations, the process or locations of the process may not make it feasible. For example, thermodynamic inhibitors are not very practical in offshore or remote production facilities due to high potential costs associated to such processes. Furthermore, at nominal conditions, a high concentration of inhibitors (10-50 wt%) is required to stop hydrate formation (Mizuta, 2006) If conditions are beyond nominal, inhibitor concentration can be extremely high (up to 60%) making such uses economically unfeasible (Koh et al., 2002)

1.6.2 Kinetic Inhibition

As opposed to thermodynamic inhibitors, kinetic inhibitors are a new and continuously
evolving technology. They inhibit the formation of hydrates by slowing down the kinetics of nucleation. Once in solution, the inhibitor adsorbs onto a crystal surface and diminishes the ability of a “guest” molecule to encage itself into the water lattice. According to Kelland et al, 2006, the kinetic inhibitors are believed to increase the activation energy barrier for the formation of hydrate nuclei by raising the surface energy of pre-nucleating aggregates (Kelland et al., 2006) Kinetic inhibitors, unlike anti-agglomerates and thermodynamic inhibitors, do not require water and hydrocarbon mixtures to be effective. The most common types of kinetic inhibitors are usually polymers and co-polymers.

1.6.3 Anti-Agglomerate Inhibition

Anti-agglomerate inhibition is also considered to be a new method of preventing hydrate formation. Like thermodynamic inhibitors, they require water and hydrocarbon mixtures to be effective. Anti-agglomerates inhibit hydrate formation by preventing the hydrate crystals from agglomerating i.e. sticking together and growing. Unlike kinetic inhibitors, they do not prevent or slow down the nucleation process. Once incorporated on a hydrate crystal, they keep the individual crystals apart and dispersed in the liquid hydrocarbon phase (Sloan, 2007) The most common types of anti-agglomerates known to date are polymers and zwitterions.

1.6.4 Advantages of Kinetic and Anti-Agglomerate Inhibition

The use of kinetic and anti-agglomerate inhibitors offer two distinct advantages. The first, is the concentration of inhibitors required for inhibition to take place. The effective amount in percentage needed for inhibition is typically in the range of 0.1-1 wt%. These ranges are much smaller compared to thermodynamic inhibitors which usually range from 10-50 wt% as previously discussed. As a result, such inhibitors have been named Low Dosage Hydrate Inhibitors (LDHI) Additionally, the costs associated in using kinetic and anti-agglomerate inhibition can be significantly reduced due to the low concentrations required to effectively prevent hydrate formation. When compared to methanol, the cost
may be reduced up to fifty percent (50%) or more (Lachet et al., 2000). Lastly, these inhibitors have a low chemical injection requirement compared to thermodynamic inhibitors (Servio, 1998).

1.7 Hydrate Promoter – Sodium Dodecyl Sulfate (SDS)

Sodium Dodecyl Sulfate (SDS), an anionic surfactant, has been used by many industries for various applications. Its typical role in industry is that of a detergent. Mainly, high concentration usages of SDS have been reported by manufactures for the removal of oily stains. Commercial products which have been found to contain high concentrations of SDS are typically engine de-greasers, floor cleaners, and car wash soaps. Toothpastes, shampoos, shaving foams and formulations of bubble bath also contain SDS, however, in smaller concentrations.

For the purpose of this research, sodium dodecyl sulfate was the only promoter used in the production of methane gas hydrate. SDS is structured as a single chain surfactant with a hydrophobic tail consisting of twelve carbon atoms, while its hydrophilic head is attached to a sulfate group. The molecular structure of SDS is thus, C_{12}H_{25}SO_4Na. Figure 1.6 illustrates a single SDS molecule.

![Figure 1.6: Molecular Structure of Sodium Dodecyl Sulfate](http://twistedphysics.typepad.com)

Due to their molecular structure, surfactants of this type have been proven to reduce surface tensions (Zhong and Rogers, 2000). Furthermore, once a minimum threshold concentration has been reached in a solution containing water, SDS has the ability to aggregate or self-assemble into micelles.
This minimum required concentration for surfactants to spontaneously form micelles is known as the critical micelles concentration (CMC). SDS micelles have been proposed as the “storage location” of large amounts of solubilized gas (Zhong and Rogers, 2000).

1.8 Hydrate Promotion

The promotion of gas hydrates has been shown to be of significant importance for industries involved in the transportation and storage of natural gas. According to several researchers, the transportation and storage of natural gas as a hydrate (HNG) can be a safer and more economical means than that of traditional methods (Benesh, 1942; Miller et al., 1946; Parent, 1948; Dubinin et al., 1979; Berner, 1992; Gramundsen and Borrehaug, 1996). Each cubic meter of gas hydrate can contain over 160 cubic meters of gas at standard temperature and pressure (Sloan, 2007). At present, natural gas is transported and stored in liquid form (LNG). However, there are significant dangers associated with such traditional methods. The most likely hazard is the possibility of massive explosions and leaks. Unfortunately, the problem with implementing the HNG method of transportation and storage is the unfavorable kinetics and low conversion of water to hydrates associated with the conversion processes (Lee et al., 2007). However, the latter difficulties can be overcome with the use of hydrate promoters. As previously discussed, the mechanism by which these promoters increase the rate of hydrate formation is the principle objective to be determined by this research. To date, two separate mechanisms have been proposed. The first was proposed by Zhong and Rogers in 2000. They proved that sodium dodecyl sulfate (SDS) was able to increase the ethane hydration rate by more than 700% (Zhong and Rogers, 2000). They speculated that this large increase in hydrate formation is due to the formation of micelles in solution. At a critical micelle concentration (CMC) of 242 ppm or greater, 60 SDS molecules agglomerate to form a micelle, trapping an ethane molecule in its cavity (center). Thus, the existence of these micelles are believed to dramatically increase the solubility of dissolved ethane.
in the liquid phase, which in turn, dramatically increases the hydrate formation rate.

The second theory proposed by Zhang et al, 2008, involves the adsorption of SDS cation at the gas-liquid interface. Upon formation, gas hydrates naturally have a negative charge in the absence of any surfactant. However, the addition of SDS decreases the negative charge or zeta potential (more negative) as the SDS concentration increases from 0.17 mM to 3.4 mM, which in turn, dramatically increasing the hydrate formation rate (Lo et al 2008; Zhang et al 2008) Promoting surfactants are usually most effective at a specific concentration. In this case, the SDS concentration is most effective at 242 ppm (For the case of Zhong and Rogers, 2000) Typically, higher concentrations result in negligible differences in hydrate formation rates (Lee et al., 2007)
2. Materials and Methods

In this section, all relevant materials and methods used to obtain all necessary data is discussed.

2.1 Reactor/Crystallizer Design

In order to produce gas hydrates, a reactor or crystallizer which can withstand extremely high pressures was designed. The reactor is made of stainless steel-316 and is an 8 inch high cylindrical unit which can withstand a maximum pressure of 20 000 kPa. The reactor unit is split in two pieces (at a horizontal cross section) The top section of the reactor is 1.88 inches thick and is bolted to the top of the remaining reactor section with 6 one half (½) inch rods, which are imbedded in the 1.75 inch thick stainless steel-316 walls. The internal diameter of the reactor is 3 inches with an internal volume of 610 ml. To ensure a proper seal between both pieces of the reactor i.e. top lid and reactor, a 3 inch OD Buna o-ring is placed in a specifically made cavity in the reactor lid. The cavity was designed specifically for this reactor so that a pressure tight seal can be created during operation. In order to ensure the production of hydrates, two windows made of polycarbonate were fitted in the front and the rear of the reactor wall. Within the wall, two (2), one eight (1/8) inch OD thick Buna o-ring are embedded to ensure a proper seal. On the surface of the reactor, Seven (7) one eight (1/8) inch female NPT ports, which penetrate through the reactor walls, were created to allowed access to the interior reactor chamber. Each of these female NPT ports are equipped with a Swagalok one eight (1/8) inch male NPT which allow a tight connection to a one eight (1/8) inch male tube unions. Of the seven ports, two located at the top and bottom of the reactor, were made to contain an Omega high accuracy RTD (± 0.3 °C) probe to precisely measure the temperature of the gas and liquid phases of the system. Of the five remaining ports, three were used for the purpose of sampling. For instance, one sample port for sampling the liquid phase, one for the gas phase and one port for the interface between the two phases i.e. vapor-liquid water interface. The addition and removing of the liquid solution from the
reactor was performed by using the liquid sample port. The remaining two ports were each independently used for gas flow into and out of the reactor. Within the reactor, a magnetic stirring rod 2.5 inches in length was used to agitate the liquid solution. With the use of an external horse shoe magnet located below the reactor, the stirring rod was coupled with the external magnet to produce a rotational speed range between 1-3000 rpm. For the purpose of this report, all experiments were conducted with a constant rotational speed of 2000 rpm. Photographs of the experimental set-up and reactor are shown in figure 2.1 and 2.2, respectively.

Figure 2.1: Photograph of Experimental Set-up Including the Reactor
2.2 Experimental Set-up

The experimental set-up consists of several key components which are required to ensure thermodynamic conditions are obtained. The need for such components is necessary in order to adequately calculate solubility. The first, is the stainless steel bath enclosure. The dimensions of the bath are 28 x 20 x 17.5 inches. It is designed to house all components which need to remain at a constant specific temperature; below ambient conditions. Such components include three stainless steel bongs and the reactor/crystallize. In order to achieve a constant temperature within the bath, an electric chiller (Neslab RTE 740) is connected via a three eights inch (3/8) plastic tubing situated outside of the bath enclosure while a copper tubing was used within the bath for efficient heat transfer. A twenty percent (20%) ethylene glycol to water solution was used to cool the desired components within the bath. Although water alone could have been used for cooling, the addition of glycol to the system safely decreased the freezing point of water to a value below that required for experimental conditions. This was done to avoid freezing of the experimental set up. A Leeson direct current permanent magnet motor was then used to agitate the twenty percent (20%) ethylene glycol water mixture. For safety purposes, the chiller cooling fluid was allowed to circulate within the tubing using a 50/50 mixture of
glycol and water solution. To ensure the desired cooling fluid temperature within the chiller is achieved and remained constant, a digital temperature reading was selected on the chiller display. Other components situated outside of the inclusion bath include Swagelok needle valves which are used for the separation of individual gas and fluid compartments (see section 2.6) For proper solubility calculations, a Baumann control valve used to control the flow of methane gas form a reservoir bong to the reactor and four 3051S Rosemount pressure transducers to indicate the pressure in each compartment. Of the four pressure transducers used in an experiment, two were used to measure differential pressures. In other words, one pressure transducers was used to measure the differential pressure between the reactor and a reactor bias while another one was used to measure the differential pressure between the reservoir and the reservoir bias. Since the differential transducer span was set from 0-2000 kPa with a reference accuracy of less 0.065% of the span (±1.3 kPa), they enabled for a very precise pressure reading. The remaining two pressure transducers were used to measure the pressure in the reactor and reservoir; each having a reference accuracy of less then 0.065% of the span (±9.0 kPa) A simple schematic representation of the experimental set-up is illustrated in figure 2.3.
2.3 Data Acquisition

In order to save all data obtained during an experiment, a computer software program which is able to extrapolate all relevant data was required. The software chosen for the extrapolation of data was the National Instruments Labview software version 7.1. Hence, all pressure and temperature data throughout the system was recorded using this program. The data is recorded at a rate of 50,000 samples per second and averaged out to supply one data point per second. The output signals from both the pressure transducers and the RTD’s are sent to SCC modules where the signal is conditioned. These signals are then introduced into a data acquisition card (DAQ) that have a 18 bit resolution. The obtained experimental data can then be saved and exported in a Microsoft Excel spreadsheet.

2.4 Materials

In order to begin experimentation, three important materials were required. The first was ultra-high purity methane gas with a 99.9+ percent purity rating. The methane gas was obtained from MEGS situated in Montreal, Quebec, Canada. The second was deionized distilled water. It was obtained in-house and provided by the department of chemical engineering. The third material required was sodium dodecyl sulfate (SDS) with a minimum purity of 99 percent GC. It was obtained from Sigma Aldrich situated in Oakville Ontario, Canada.

2.4.1 Preparation of Sodium Dodecyl Sulfate (SDS)

A solution of deionized distilled water and sodium dodecyl sulfate was prepared and tested with two different concentrations. The two separate concentrations were required to further prove whether SDS micelles had an impact on solubility in a methane hydrate system. Since the CMC of SDS was determined to be 242 ppm (Zhong and Rogers, 2000), one concentration was chosen below the CMC (31 ppm) and one was chosen above (253 ppm). Using a weight scale with an accuracy of 0.01 grams, a specific amount of SDS powder was weighed and placed in a flask which already contained the desired
amount of deionized distilled water. The flask was then capped and shaken by hand until all of the SDS was dissolved. Both concentrations of 31 ppm and 253 ppm were prepared using the above methodology.

2.5 Experimental Conditions

Two types of experiments were conducted to obtain viable data. Solubility and kinetic experiments are two types of experiments used to determine the solubility and dissolution rate of methane, and the growth rate of methane hydrate, respectively. However, for the purpose of this study, both the solubility and kinetic experiments were used to determine the solubility of the liquid water phase. The growth rate of methane hydrate was only used for verification purposes as it was beyond the scope of this work.

2.5.1 Solubility Experiments

To determine the solubility and dissolution rate of methane, solubility experiments must be performed. Traditionally, solubility experiments are performed below the three phase equilibrium line i.e. below the hydrate - liquid water - vapour points established by Deaton and Frost (Deaton and Frost, 1946) The reason for this is due to the formation of methane hydrate. If the solubility experiment is performed above the three phase equilibrium line, the liquid phase will supersaturate with the gaseous component and ultimately form methane hydrates. This makes it impossible to properly determine the solubility of the liquid phase using gas consumption plots obtained from using the Trebble-Bishnoi equation of state (Trebble and Bishnoi, 1987) (see section 2.7) Therefore, all experiments conducted with the Trebble-Bishnoi equation of state procedure, to determine the solubility of the liquid phase, were performed at various temperatures and pressure below the three phase equilibrium line.

Alternatively, the restrictions imposed by the latter procedure are eliminated when performed with the analytical flask technique. That is, the operating conditions are no longer restricted to
conditions below the three phase equilibrium line. Experiments can thus be performed at any condition, above or below the equilibrium line i.e. in the presence or absence of gas hydrates. The reason for this, is that a liquid sample is physically taken form the reactor and analyzed as opposed to using an equation of state to predict the number moles consumed. Therefore, if the system to be tested is in equilibrium, a liquid sample (liquid bulk) that does not contain hydrates can be extracted and analyzed to accurately determine the number of moles in the liquid phase, which is in turn, the solubility. If experimentally required, both techniques were performed and compared for analysis.

2.5.2 Kinetic Experiments

Kinetic experiments have been used for a variety of experiments to determine the growth rate of hydrates. To properly determine the growth rate of hydrates, operating conditions must be above the three phase equilibrium line reported by Deaton and Frost (Deaton and Frost, 1946) If such conditions are not met, methane hydrates will be unable to form, producing no growth. For the purpose of this work, kinetic experiments were performed solely for verification purposes. The growth rate of hydrate was quickly investigated to determine whether the concentrations of SDS to be examined correspond to what was seen in literature. Since Zhong and Rogers reported a significant growth rate of ethane hydrates at an SDS concentration above the CMC (Zhong and Rogers, 2000), a verification was performed with methane gas at concentration above and below the CMC. The results obtained form this test is included in section 3 of this report.

2.6 General Procedure

In order to calculate solubility, the experimental set up was divided into four different compartments. This was done so that the correct mole consumption can be accurately and precisely determined. The four compartments are,

1) The isolation of the reactor/crystallizer
2) The isolation of the reactor bias

3) The isolation of the reservoir

4) The isolation of the reservoir bias

Prior to an experiment, the reactor was washed by injecting and purging of distilled water. Using the reactor liquid sample port needle valve, approximately 350 ml of distilled water was injected into the reactor. The magnetic stirrer was then turned on to allow agitation for approximately 1 minute. Subsequently, the magnetic stirrer was then turned off and the reactor liquid sample port needle valve was closed. The reactor was then pressurized to several hundred kilo-pascals to obtain a positive displacement. The reactor liquid sample port was then opened to allow the distilled water to flow out of the reactor and into a beaker. The above method was repeated a total of 5 times prior to each experiment. Once the reactor was determined to be clean, 300 ml of distilled water was injected and allowed to cool for approximately 2 hours. At the start of an experiment, all compartments (except the reactor compartment) which are isolated by Swagelok needle valves, have their respective inlet needle valves in an open position. Methane gas is then allowed to flow into each compartment until a certain pressure is attained. Upon attaining the desired operating pressure, the methane gas inlet valve is turned off, allowing all three compartments to reach equilibrium with each other. It is noteworthy to mention that to adequately use the Baumann control valve, a positive displacement in pressure is needed between the reservoir and the reactor. Therefore, to ensure a proper flow direction from the reservoir to the reactor, the pressure within these three compartments must always be higher or greater than that of the reactor. Therefore, throughout all experiments, the above mentioned compartments were always approximately 1000 kPa greater than that of the reactor. Once all three compartments were allowed to reach equilibrium, their respective inlet valves were closed. Finally, before pressurization of the reactor can be performed, trapped air within the reactor must to be evacuated. This was done by pressurizing the reactor 3 times to a value of 1000 kPa and then purged. Upon completion, the reactor was
pressurized to the desired operating pressure and allowed to reach equilibrium. At this point, an experiment can now be performed.

2.7 Experimental Procedure using the Trebble-Bishnoi Equation of State

Upon completion of the general procedure, the DAQ was turned to an “on” position to allow the recording of all relevant data including all pressures in each compartment, gas and liquid reactor temperatures and reservoir gas temperature. At this point, the control valve is set to a specific value to allow the replacement of dissolved methane gas in the reactor, from the reservoir. The stirring mechanism was then turned on, agitating the distilled water at a speed of 2000 rpm. The experiment was deemed completed once the dissolution rate of methane completely stopped. Once completed, the reservoir temperature and reservoir differential pressure data was saved and compiled into an excel spreadsheet and allowed for interpolation using a program that was written in MATLAB that employed the Trebble-Bishnoi equation of state (Trebble and Bishnoi, 1987) Since the data obtained was in terms of temperature and pressure, the MATLAB program (Trebble-Bishnoi equation of state) converted all data in terms of moles consumed. Hence, a mole consumption plot was obtained for every experiment.

2.8 Experimental Procedure using the Analytical Flash Technique

The analytical flash technique is a technique that was first used by Servio and Englezos (Servio and Englezos, 2002) to determine the solubility of methane in liquid water in a high pressure bomb. This technique requires a liquid sample be taken directly from the reactor at the specific operating conditions. Hence, upon completion of the general procedure, the control valve is set to a specific value to allow the replacement of dissolved methane gas in the reactor, from the reservoir. The stirring mechanism was then turned on, agitating the distilled water at a speed of 2000 rpm. While the experiment is ongoing, two high pressure bombs used for the later part of the experiment, were vacuumed of any gas or liquid to eliminate the possibility of contamination. Once the dissolution rate
of methane into the liquid was completed, the stirring mechanism was stopped, in turn producing equilibrium conditions. The control valve was then reset to a set point of 2% higher then the actual present value so that it would not over compensate the pressure drop obtained from connecting the high pressure bomb to the liquid sample port. The first high pressure bomb was then connected, using a Swagelok quick connection, to the reactor liquid sample port. The Swagelok needle valve connected to the liquid sample port was then opened followed by the opening of the Swagelok needle valve connected to the sample bomb. The flow rate out of the reactor and into the sample bomb is extremely high due to the large pressure differential between the reactor and the sample bomb. Therefore, approximately 2 seconds upon opening of the sample bomb needle valve, the valve is quickly closed. The initial liquid sample port needle valve is then subsequently closed. Since the liquid sample port line is now clear of any possible contaminants, the initial sample bomb is disconnected and discarded from the liquid sample port and quickly replaced by the second liquid sample bomb. The valve sequence required to obtain a sample from the reactor is then repeated so that the actual sample in the second bomb can be tested. Once the liquid sample from the reactor is obtained in the liquid sample bomb, it is attached to a Ruska gasometer, which brings the contents of the bomb at room temperature and pressure into its two corresponding phases, liquid and gas. As the bomb reaches atmospheric pressure, methane once dissolved in the liquid phase is allowed to escape into its corresponding gas phase. The amount of methane gas escaping from the liquid is allowed to enter a chamber of the Ruska gasometer where a piston is used to determine the volume of gas. The volume of gas required to come out of the liquid phase so that atmospheric pressure and room temperature can be reached is then recorded. The volume of gas is then converted to moles of methane gas using the ideal gas law namely,

\[ P V = z n R T \]  

(1)

where P, V, z, n, R and T is the atmospheric pressure, the volume of methane gas in the gasometer, the compressibility factor for CH₄, the number of moles of methane gas, the universal gas constant and the
room temperature, respectively. Since the amount of water in the high pressure bomb is known, the amount of methane in the liquid bulk at atmospheric pressure can be determined. Upon obtaining the number of moles of methane gas from the ruska chamber and the number of moles of methane in the liquid at atmospheric pressure, one can calculate the solubility of methane since the total number of moles of water and SDS used (if required) is known.

Two sets of data were obtained using the analytical flask technique. The first, was performed with ultra high pure methane gas and distilled deionized water. This was done so that it can be used as a baseline when compared to ultra high pure methane gas, distilled deionized water and SDS. Furthermore, the above data was used to verify the accuracy of the experimental set up as it was compared to values obtained by Servio and Englezos (Servio and Englezos, 2002) All values obtained were in the range of 5% error or less. The second set of data was performed using ultra high pure methane gas, distilled deionized water and SDS. The purpose was to determine whether SDS micelles can trap methane gas and dramatically increase the solubility of the liquid phase.

2.9 Experimental Shutdown

An experimental shutdown of all equipment which can potentially cause harm to an individual or its surrounding environment is necessary to ensure safety. Upon completion of an experiment, the reactor, reactor bias, reservoir and reservoir bias were all depressurized to standard atmospheric pressure. The methane gas was allowed to flow through the exit piping of the experimental set-up directly into the M.H. Wong building exit ventilation system. The liquid solution present in the reactor was removed by utilizing the pressure gradient between the reactor and atmospheric pressure. Therefore, before completely depressurizing the reactor to atmospheric pressure, the liquid sample port valve was opened to allow the removal of the reactor liquid. Once all of the water was removed form the reactor, the liquid sample port valve was closed to allow the reactor gas to escape into the exit
ventilation system. The reactor was then cleaned and prepped for the next experiment.
3. Results and Discussion

In this section, all data obtained during the course of this research is analyzed and discussed.

3.1 Experimental Data Obtained Using the Trebble-Bishnoi Equation of State

The data presented in this work was performed at operating conditions below the three phase equilibrium line as reported by Deaton and Frost i.e., All of the experiments were performed with an SDS concentration of 31 ppm which is below the CMC. These experiments were conducted to determine whether a minute concentration of SDS is able to increase the solubility of methane in water. In order to fully examine the non-hydrate forming region, two separate operating pressures were chosen for every temperature to be tested. For example, at a temperature of 2°C, one experiment was conducted at a pressure of 1500 kPa while another experiment was conducted at a pressure of 2900 kPa. Hence, the idea was to select a temperature and perform an experiment using a pressure 1500 kPa below the three phase equilibrium line and another using a pressure of 100 kPa below the equilibrium line. The data obtained is presented below.
Figure 3.1: Mole Consumption Plot of Methane at $2^\circ$C and 1500 kPa

Figure 3.2: Mole Consumption Plot of Methane at $2^\circ$C and 2900 kPa
Figure 3.3: Mole Consumption Plot of Methane at 4°C and 2100 kPa

Figure 3.4: Mole Consumption Plot of Methane at 4°C and 3500 kPa
Figure 3.5: Mole Consumption Plot of Methane at 8°C and 4200 kPa

Figure 3.6: Mole Consumption Plot of Methane at 8°C and 5600 kPa
In order to determine the solubility of methane in water or of methane in SDS and water, by definition, the system must first reach equilibrium. Therefore, the solubility values from Figures 3.1 through 3.7 is obtained when the slope of the curve reaches zero. However, the most important result attained from these experiments is that the solubility of methane in water and that of SDS (31 ppm) and water converge to the same value, for the same operating conditions. This trend was clearly observed in all experiments and is illustrated in Figures 3.1 through 3.7. Therefore, the main conclusion obtained from this type of experimentation is that the solubility of methane in water with SDS at a concentration of 31 ppm is equivalent to the solubility of methane in water alone.

A second, less significant observation obtained by analyzing figures 3.1 through 3.7, is the rate of methane consumed in water versus the rate of methane consumed in water and SDS (31 ppm). Although it seems that the rate of methane consumed in water alone is higher than that of methane with SDS (31 ppm) and water (from figures 3.1 through 3.7, the blue curve is always a higher value than the red curve), it is however, impossible to conclude such an observation based on the extremely small values separating the two curves at any given time. Furthermore, two replicates for each curve is not enough to statistically prove this trend. Thus, more replicates would have to be performed to justify the observation. With this noted, the solubilities obtained for each specific operating condition are equivalent regardless of which solution used (water with SDS at a concentration of 31 ppm or water alone).

3.2. Additional Experimental Data Using the Trebble-Bishnoi Equation of State

Since the solubility experiments conducted using SDS with a concentration of 31 ppm and water were equivalent to that of water alone, the next step was to perform an experiment for which the concentration of SDS was greater than that of the CMC. This was done to determine whether the micelles formed within the solution are capable of trapping methane gas, ultimately increasing the
solubility. The following experiment was performed at a temperature of 4°C and a pressure of 3500 kPa.

![Mole Consumption Plot for Methane at 4°C and 3500 kPa Using Two Different SDS Concentrations](image)

**Figure 3.7:** Mole Consumption Plot for Methane at 4°C and 3500 kPa Using Two Different SDS Concentrations

As can be seen from figure 3.7, the average mole consumption of methane in water alone (control experiment) was compared to that of water and SDS with a concentration of 31 ppm (below the CMC) and that of water and SDS with a concentration of 253 ppm (above the CMC) According to Zhong and Rogers, the solubility of methane in water and SDS with a concentration above the CMC should have a drastic increase in solubility due to the presence of micelles in solution, trapping all of the excess methane gas. However, as observed in figure 3.7, this is not the case. Instead, the solubility of methane in water and SDS at any concentration above or below the CMC does not alter the solubility. Therefore, there is no effect on solubility regardless of SDS concentration used for operating conditions below the three phase equilibrium line (non-hydrate forming region)

To determine whether the rate of hydrate formation is influenced by the addition of SDS at a
concentration of 253 ppm without disrupting or altering the solubility, an experiment was conducted at a temperature of 4°C and 4700 kPa (above the three phase equilibrium line) The data is plotted and shown below.

![Mole Consumption Plot for Methane at 4°C and 4700 kPa](image)

**Figure 3.8:** Mole Consumption Plot for Methane at 4°C and 4700 kPa Using Two Different SDS Concentrations

As can be seen from figure 3.8, it is evident that the concentration of methane, prior to the onset of hydrate formation, in water alone (control sample) and water and SDS at both specific concentrations above and below the CMC, are equivalent. Most importantly, it is clearly observed, that at an SDS concentration of 253 ppm, the rate of hydrate formation is significantly increased while the solubility of methane remained the same for both the control sample and the solution with an SDS concentration of 31 ppm (prior to the onset of hydrate formation) It is noteworthy to mention that this technique, as previously mentioned in this report, can only accurately determine the solubility of methane in any solution up to the onset of hydrate formation. Beyond this point, there is no way to predict the solubility of methane in the solution during hydrate growth using this method. As for the
discrepancy between the three experiments prior to the onset of hydrate formation, the same argument applies as previously discussed since more replicates are required.

### 3.3 Experimental Data Obtained Using the Analytical Flash Technique

The analytical flash technique was used to determine the solubility of the liquid bulk in the presence of hydrates and during hydrate formation. In essence, this technique can accurately determine solubility while operating above the three phase equilibrium line. The data obtained using this technique is illustrated in table 3.1 below.

<table>
<thead>
<tr>
<th>Experiment (#)</th>
<th>SDS Concentration (ppm)</th>
<th>Average Temperature (K)</th>
<th>Average Absolute Pressure (kPa)</th>
<th># of Experimental Replicates</th>
<th>Average Solubility (moles)</th>
<th>Solubility Abs. Avg. Dev. wrt Replicates (%)</th>
<th>Solubility Abs. Avg. Dev. wrt Servio* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NA</td>
<td>281.54</td>
<td>5 000</td>
<td>3</td>
<td>1.526 x10^-3</td>
<td>1.7</td>
<td>0.13</td>
</tr>
<tr>
<td>2</td>
<td>NA</td>
<td>283.28</td>
<td>6 500</td>
<td>3</td>
<td>1.732 x10^-3</td>
<td>1.2</td>
<td>0.7</td>
</tr>
<tr>
<td>3</td>
<td>253</td>
<td>282.15</td>
<td>6 500</td>
<td>3</td>
<td>1.847 x10^-3</td>
<td>2.3</td>
<td>0.15</td>
</tr>
<tr>
<td>4</td>
<td>253</td>
<td>280.32</td>
<td>6 500</td>
<td>3</td>
<td>1.637 x10^-3</td>
<td>4.7</td>
<td>4.5</td>
</tr>
<tr>
<td>5</td>
<td>253</td>
<td>277.32</td>
<td>5 000</td>
<td>3</td>
<td>1.340 x10^-3</td>
<td>3.9</td>
<td>2.9</td>
</tr>
</tbody>
</table>

*Note: Data is compared to work of Servio and Englezos, 2002*

From Table 3.1 above, each experiment was given an experiment number for identification purposes. The solutions which contained only distilled deionized water is referred to as having an SDS concentration of NA. If SDS was present in the distilled deionized water, the concentration was specified. Operating conditions including the average temperature and average absolute pressure is also listed in the above table. For each experiment, 3 replicates were conducted to ensure accuracy. The average solubility of all three replicates is reported under the column titled “Average Solubility”. In calculating the solubility, the absolute average deviation with respect to the replicates is reported as well as the absolute average deviation with respect to solubility values obtained from Servio and Englezos, 2002. The values reported by Servio and Englezos are values associated with using distilled
deionized water at several different operating conditions covering all three regions of the Deaton and Frost three phase equilibrium curve. Therefore, the data previously reported by Servio and Englezos was used as a means of reference for this work. Experiments 1 and 2 are examples of these. For experiments 1 and 2, no SDS was used, allowing a direct data comparison to Servio and Englezos. The results obtained are almost identical, with the maximum absolute average deviation of 0.7%. It is thus justifiable to assume that the procedure and experimental set up operated accordingly, and that each value reported by Servio and Englezos can be used as a means of reference when compared to experiments performed with SDS.

Experiments 3, 4 and 5 were conducted with solutions containing SDS with a concentration of 253 ppm. The results obtained are illustrated in Table 3.1. The maximum absolute average deviation obtained with respect to the replicates is 4.7% for experiment 4. It is important to note that any value less than 5% is regarded as a very small error since the solubility values are in thousandths of a decimal or less. Therefore, a small deviation can result in large percentage errors. Since all values are less than 5%, the experimental results are regarded as being accurate. The most significant result obtained from table 3.1 is the compared solubility values from experiments 3, 4 and 5. It is evident that the absolute average deviation with respect to values obtained from Servio is a maximum of 4.5%. This result can only conclude that solubility of the liquid bulk from a solution containing SDS is equivalent to that containing distilled deionized water alone. If the solubility of the bulk were to increase as speculated by Zhong and Rogers, the absolute average deviation would be significantly higher. However, this is not the case. Hence, the solubility of the bulk does not increase with a concentration of SDS above the CMC but instead, remains constant. This result further confirms and compliments the results obtained using the Trebble-Bishnoi Equation of State.

Although Zhong and Rogers believed that SDS micelles were the driving force behind the dramatic increase in hydrate formation, the above data confirms otherwise. Hence, the only viable
theory accepted by literature, which has not yet been dis-proven, involves the use of a zeta-potential which was previously discussed in this report.
4. Conclusion and Recommendations

4.1 Conclusion

The solubility of methane in SDS and water in both the hydrate and non-hydrate forming regions was investigated using two methods, using the Trebble Bishnoi equation of state and the analytical flask technique. The resulting solubility was then compared to that of distilled deionized water to determine whether SDS can significantly increase the solubility of methane in water by trapping methane gas within micelles (Zhong and Rogers, 2000). Solubility results show that the amount of methane dissolved in SDS (at two separate concentrations of 31 ppm and 253 ppm) and water is equivalent to that of water alone operating at similar conditions. Therefore, the solubility of methane in SDS and water does not increase but rather remains constant and consistent to that of water alone. Finally, of the two theories that were published in literature concerning the possible mechanism for the dramatic increase of hydrate formation in the presence of SDS, the theory postulated by Zhong and Rogers is invalid. Therefore, although experimental verification must still be accomplished to validate the increase in zeta potential, the remaining theory postulated by Zhang et al, 2008 is the only valid theory accepted to date.

4.2 Recommendations

According to the findings presented in this report, work should be continued to evaluate the theory postulated by Zhang et al. Hence, possible work involving the determination of surface tension at the gas-liquid interface for distilled deionized water and a solution consisting of distilled deionized water and SDS at varying concentrations. Comparisons should then be made to determine the possible role of surface tensions. The determination of hydrate polarity including the addition of SDS at various concentrations should also be further investigated. Furthermore, research should evolve into the area
involving SDS Gemini surfactants. This new technology where the linking of two SDS molecules using a spacer could be the next generation of surfactants since it can be hypothesized that a much smaller concentration of SDS Gemini surfactant could obtain the same results as SDS at a higher concentration. Surface tension and polarity experiments should then also be conducted using the SDS Gemini surfactant.
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